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(71) Applicant *(for all designated States except US)*: SOLA INTERNATIONAL, INC. [US/US]; 2420 Sand Hill Road, Menlo Park, CA 94025 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: RAM, Sunder [US/US]; 22 Dupree Court, Petaluma, CA 94954 (US). MCCARTHY, Anthony [IE/US]; 1386 23rd Avenue, San Francisco, CA 94122 (US). GRAF, Herbert [DE/US]; 6945 C Berry Lane, Sebastopol, CA 95472 (US).

(74) Agent: PETERSON, James, W.; Burns, Doane, Swecker & Mathis, L.L.P., P.O. Box 1404, Alexandria, VA 22313-1404 (US).

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(54) Title: WATER-BASED PAD PRINTING INK COMPOSITION

(57) Abstract

A transfer-pad printing aqueous composition comprising effective amounts of a water soluble polymer, an opacifier, and a dispersant and optionally a colorant and/or release agent is provided. The composition is particularly suited for use with silicone rubber transfer-pads to print alphanumeric patterns on curved or spherical surfaces such as opthalmic lenses.

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WATER-BASED PAD PRINTING INK COMPOSITION

FIELD OF THE INVENTION

The present invention relates generally to a transfer-pad printing ink composition preferably comprising a waterborne vinyl resin, an opacifier, a release agent, a dispersant and a colorant. The ink composition is particularly suited for use with silicone rubber transfer pads to print alphanumeric patterns on curved or spherical articles such as ophthalmic lenses. The ink formulation is compatible with the pad surface so the pad precisely transfers the design to a surface that is receptive to the ink which is removable with water.

BACKGROUND TO THE INVENTION

Pad or transfer-pad printing is a well established method for transferring ink in the form of a thin design to a shaped surface such as one having a rounded or otherwise irregular contour. This technique differs from traditional printing in that it does not rely on a typeface in transferring the design. Pad printing has been used commercially for many applications such as (1) printing patterns on light bulbs, watch faces, and golf balls, (2) printing circuits on dielectric substrates, (3) imprinting bar codes, and (4) marking glass or plastic ophthalmic lenses for subsequent identification in prescription-filling optical laboratories.

There are a number of commercial transfer-pad printing systems available. For example, systems are obtainable from Trans Tech America, Inc., Schaumberg, IL. Markem Corporation, Keene, NH; Tampo Print GmbH, Munich and Stuttgart, Germany. Transfer-pad printing devices are described, for example, in 4,060,031, 4,282,807, 4,615,266, 4,779,531, 4,803,922 and 4,856,670. Though these systems are automated and geared to accurately transfer the pattern from a printing block (cliché), which contains the ink design to be transferred, a critical step in the process involves accurately picking up the ink design from the cliché, without altering the design as it lays on the pad prior to transfer to a receiving surface.

Reproducing the design on a cliché on a substrate depends upon the ability of the ink composition deposited in the cliché to effectively wet the surface of the transfer-pad. If the ink composition does not properly wet the pad surface, the pad will not completely pick up the ink in the design provided in the cliché. Alternatively, the pad may pick up the ink design by suction of a sufficient mass only to have the design break up (or bead up) on the pad because of an incompatibility between the ink and the pad surface prior to transference of the design to the desired surface. To address this problem, WO 92/20005 described a modified transfer-pad printing composition comprising either a latex or a solution coating composition which includes a monomeric or polymeric hydroxylated and/or carboxylated surface active wetting agent.

Following transfer of the ink composition, printing is complete when the ink dries to form the design. In this regard, some commercially available organic solvent-based inks must be dried and cured at elevated temperatures. The volatile organic compounds in organic solvent-based inks raise environmental concerns not only because of their presence but also because acetone or another organic solvent is required to remove the print thereby further aggravating the problem. Finally, it has also been observed that some organic solvent-based inks cause a phenomenon referred to as "ghosting," where the ink composition leaves an impression on the surface of a plastic substrate after the ink (e.g., design) has been wiped off.

SUMMARY OF THE INVENTION

The present invention is based in part on the discovery of a transfer-pad aqueous ink composition comprising a marking ink in a waterborne vinyl resin dispersion that is compatible with pad surfaces including those made of silicone rubber. The ink composition, in the shape of an alphanumeric or any geometric pattern, can be precisely imprinted on the pad surface; thereafter, the design can be precisely transferred to another surface that is receptive to the ink.

In one aspect, the invention is directed to an aqueous coating composition suitable for use in transfer-pad printing that comprises a water soluble polymer; an opacifier; and a dispersant.

Preferably, the soluble polymer is a vinyl resin and the ink composition includes a colorant to enhance the appearance of the finished pattern. When the transfer pad is made of silicone rubber, the composition includes a release agent.

In another aspect, the invention is directed to a transfer-pad printing method of printing a pattern of a liquid coating from a cliché to a substrate surface wherein the liquid coating comprises the above described aqueous ink composition. In yet another aspect, the invention is directed to articles including, for example, ophthalmic lenses, fabricated by this process.

In a preferred embodiment, the inventive aqueous ink composition does not include an organic solvent which avoids the hazards associated with organic solvent-based inks. In addition, the inventive ink composition overcomes the deficiencies of conventional aqueous ink compositions which have not been satisfactory. Specifically, prior art aqueous inks tend to bead up on the silicone rubber pad surface thereby breaking up the design sufficiently so that the resultant imprinted product is a poor replica of the original design. Furthermore, conventional aqueous marking ink solutions generally form very light and not well defined imprints that lack body and substance. For these reasons they fail to meet the requirements of a precision manufacturing environment where readability, clarity, abrasion resistance, sturdiness and moisture resistance are necessary.

A feature of the inventive water-dispersible ink is that it can dry at room temperature (about 22°-25°C) in only a few seconds, or less time when air assisted, to form good quality, well-defined prints that are comparable to those formed from organic solvent-based inks. The prints are also abrasion resistant so that articles (e.g., ophthalmic lenses) that are imprinted can be safely packaged and shipped.

Another feature of the invention is that the imprinted ink marks can be readily removed by wiping with cold water.

A further feature is that the aqueous ink composition can imprint patterns on ophthalmic lenses that are uncoated, coated for abrasion resistance and/or anti-reflectivity. Plastic lenses are often coated with, for example, films derived from polysiloxane, acrylate, epoxy, or urethane based compounds for abrasion resistance and with multilayer films comprising silica, titania and/or niobia for anti-reflectivity.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention is directed to water-based ink compositions for marking irregular surfaces. The ink compositions can be employed to imprint any article which can be imprinted by transfer-pad printing. The invention will be illustrated with printing on ophthalmic lenses. In the case of ophthalmic lenses, the markings are used in the production of lens products. Specifically, the markings identify reference points on a lens, e.g., fitting cross, prism point, near measurement etc., which guide laboratory personnel in grinding, polishing and otherwise fitting the prescription to that required for the final eyeglass product.

Ophthalmic lenses are fabricated from materials having superior structural and optical properties. Crystalline quartz, fused silica, soda-lime silicate glass, and plastics such as from polymers based on allyl diglycol carbonate monomers (available as CR-39™ from PPG Industries, Inc., Hartford, CT), diacrylate or dimethacrylate compounds as described in U.S. Patents 5,373,033 and 4,912,185, both incorporated herein, and which are available as SPECTRALITE™ from Sola Optical USA, Inc. Petaluma, CA, and polycarbonates such as LEXAN™, available from General Electric Co., are preferred substrate materials for ophthalmic lenses (including sunglasses). Preferred ophthalmic lenses also include laminated lenses that are fabricated by bonding two lens wafers (i.e., a front wafer and a back wafer) together with a transparent adhesive. Laminated lens wafers are described, for example, in U.S. Patents 5,149,181, 4,857,553, and 4,645,317 and U.K. Patent Application,

GB 2,260,937A, all of which are incorporated herein. Suitable substrates further include glass ophthalmic lenses, as described, for instance, in U.S. Patents 3,899,315 and 3,899,314, both of which are incorporated herein. As used herein, the term "lens" refers to both single integral body and laminated types.

The lens can be uncoated or coated for abrasion resistance or antireflectivity. Ophthalmic lenses, particularly plastic ones, that are coated with a polymeric abrasion or scratch resistance coating that may be about 1 μm to about 12 μm thick are also suitable substrates. The thickness of the polymeric scratch resistance coating will depend, in part, on the substrate material. Generally, plastic materials such as polycarbonates will require thicker coatings.

Suitable lenses may also have an antireflection coating which refers to a substantially transparent multilayer film that is applied to optical systems (e.g., surfaces thereof) to substantially eliminate reflection over a relatively wide portion of the visible spectrum, and thereby increase the transmission of light and reduce surface reflectance. Known anti-reflection coatings include multilayer films comprising alternating high and low refractive index materials (e.g., metal oxides) as described, for instance, in U.S. Patents 3,432,225, 3,565,509, 4,022,947, and 5,332,618, all of which are incorporated herein. The thickness of the AR coating will depend on the thickness of each individual layer in the multilayer film and the total number of layers in the multilayer film. The AR coating can include any number of layers. Preferably, the AR coating for the ophthalmic lens has about 3 to about 12 layers, more preferably about 4 to about 7 layers, and most preferably about 4 layers. Preferably, the AR coating is about 100 to about 750 nm thick. For use with ophthalmic lenses, the AR coating is preferably about 220 to about 500 nm thick. A suitable anti-reflection coating is described in U.S. Patent Application Serial No. 08/487,365 by Machol, entitled "Anti-reflection Coating", of common assignee, filed on June 7, 1995, which is incorporated herein.

However, before describing the invention in further detail, the following terms will be defined.

The term "soluble polymer" refers to suitable water soluble polymers that are compatible with the other components of the ink composition to form an aqueous polymer mixture which produces a polymer composition with the other components impregnated therein when the mixture is dried. Soluble polymers include, for example, suitable urethanes, acrylates, epoxies, cellulose, and vinyl derivatives. Specific examples, include, polyurethanes available as NEOREZ™ from Zeneca Resins, Wilmington, MA, styrene acrylates available as JONCRYL™ from Johnson Wax Co., Racine, WI, hydroxypropylcellulose available as KLUCEL™, cellulosic polymers available as AMBERGUM™ both from Aqualon Co., Wilmington, DE, and aqueous vinyl polymer mixtures that are available under the designations AW850, AW100, AW870, AW875 and WBV100 from Union Carbide, Danbury, CT. Preferred soluble polymers are thermoplastic. Preferred soluble polymers for the ink composition, comprise vinyl resins which are vinyl polymers or copolymers that are soluble in water at room temperature. The presence of an aqueous colloidal dispersion of said vinyl resins in the ink composition is critical in achieving the desired flowability, printability and durability of the marking ink. The ink also has good redispersibility characteristics and is easy to remove. Preferably, the vinyl resin is a vinyl chloride copolymer. Suitable vinyl chloride copolymers are available as a waterborne vinyl dispersant such as, for example, the UCAR™ waterborne vinyls (available from Union Carbide, Danbury, CT). A preferred waterborne vinyl resin dispersion is AW-850™, which contains about 40% solids, is available from Union Carbide. The soluble polymer typically comprises from about 10% to about 30%, preferably about 15% to 25%, and more preferably about 20% to 25% of the ink composition when first formulated, that is, prior to drying. (All percentages herein are on a weight basis). Another preferred waterborne vinyl resin dispersion is WBV 100 which contains about 50% solids. This soluble polymer comprises from

about 10% to 30%, preferably about 15% to 25%, and more preferably 20% to 25% of the ink formulation.

The term "opacifier" or "opacifying agent" refers to any suitable substance that imparts strength, durability and/or sharpness to the design or pattern created on a substrate surface when the ink composition has dried. In addition, it appears that the opacifying agent also improves the consistency and texture of the ink so that it can be readily transferred from the cliché to the articles surface by the transfer pad. Preferred opacifiers are inorganic materials such, for example, titanium dioxide, aluminum oxides, aluminum silicates, and silica. Titanium dioxide is preferred because it is less abrasive and creates superior appearing, well-defined designs and marks. When a colorant is used in the ink composition, the TiO_2 opacifier creates a white background which enhances the color of the colorant. The opacifying agent typically comprises from about 5% to 45%, preferably from about 5% to 30%, and more preferably from about 10% to 20% of the aqueous ink composition.

The term "dispersant" refers to any suitable substance which acts as a wetting agent to disperse the ink components especially the opacifier (and colorant which is optional) to form an aqueous mixture wherein the undissolved fine solid particles are uniformly distributed and separated. Preferred dispersants include, for example, water-reducible alkyds, acrylics, polyesters, epoxies, and mixtures thereof. DISPERSE-AYD W-22™ (available from Daniel Products, Jersey City, N.J.) is a preferred dispersant. The dispersant typically comprises from about 0.5% to 5.5%, preferably from about 1% to 5%, and more preferably from about 1% to 2.5% of the aqueous ink composition.

The term "release agent" refers to any suitable substance that acts as a lubricant to render the aqueous ink composition more readily transferable from the cliché to the silicone rubber transfer pad and from the pad to the substrate (e.g., lens) surface. Silicone rubber material is described, for example, in WO 92/20005. Suitable release agents include, for example, silicone fluids. A preferred release agent is a silicone fluid available as SF1188™ from General

Electric Co., Waterford, NY. The release agent typically comprises from about 10% to 30%, preferably from about 12.5% to 27.5% and more preferably about 15% to 20% of the aqueous ink composition.

The term "colorant" refers to suitable substances which impart color to another material or mixture. Colorants are used as desired to render uniqueness to the mark, e.g., "color coding." In addition, colorants provide improved legibility with surface saver tapes in lens surfacing process. Colorants typically comprise either nonsoluble inorganic and soluble organic dyes. Preferred colorants include Erioglaucine (turquoise blue) and Tartrazine (yellow) both available from Aldrich Chemical Co., Milwaukee, WI. When present, the colorant comprises from about 0.25% to 7.5%, preferably from about 0.5% to 5%, and more preferably from about 0.5% to 2.5% of the ink composition.

METHODOLOGY

The inventive ink composition can be employed in conventional transfer-pad devices which typically comprise a silicone rubber pad for transferring an ink pattern from a cliché ink source and printing the design onto the surface of an article (e.g., lens surface). Excess ink is removed from the cliché with a doctor blade. Typically, the aqueous ink composition comprises about 20% to 50% water, preferably about 25% to 45%, and more preferably about 35% to 45%. The composition is thixotropic and has a viscosity of about 1,000 cp to 20,000 cp, preferably about 5,000 cp to 15,000 cp, and more preferably about 7,500 cp to about 12,500 cp at room temperature.

Markings on plastic ophthalmic lenses that identified reference points on each lens were formed using Tampo Print Hermetic transfer-pad printing device models 61 and 90. The devices were available from Trans Tech America, Inc., Schaumberg, IL and adapted for fabricating ophthalmic lenses.

The following Examples 1-6 describe representative preferred formulations of the inventive aqueous ink composition:

Example 1: To 54.3 g of AW850 (soluble polymer) add 10.81 g of de-ionized water under stir. To this add 1.63 g of DISPERS-AYD W22 (dispersant). 0.81 g Erioglaucine and 0.11 g Tartrazine (colorants) are then added and the mixture is stirred for 15 minutes. Next add 14.12 g of titanium dioxide and continue stirring for a further 2 hours. Finally, add 18.19 g of the SF1188 (release agent) and stir for 2 more hours. This formulation achieves a teal colored ink.

Example 2: The same mixing procedure as Example 1 except replace the AW850 with 54.3 g of WBV110.

Example 3: To 60.88 g of AW875 add 1.79 g of DISPERS-AYD W22 under stir. 0.9 g Erioglaucine and 0.11 g Tartrazine are then added and the mixture is stirred for 15 minutes. Next add 15.92 g of titanium dioxide and continue stirring for a further 2 hours. Finally, add 20.52 g of the SF1188 and stir for 2 more hours. The formulation achieves a teal colored ink.

Example 4: To 64.31 g of AW875 add 1.29 g of DISPERS-AYD W22 under stir. 0.96 g of Tartrazine is then added and the mixture is stirred for 15 minutes. Next add 15.43 g of titanium dioxide and continue stirring for a further 2 hours. Finally, add 18.0 g of SF1188 and continue stirring for 2 hours. The formulation achieves a yellow colored ink.

Example 5: The same mixing procedure as Example 4 except replace the AW850 with 64.31 g of WBV110.

Example 6: The same mixing procedure as Example 4 except replace the AW850 with 64.31 g of AW875.

After lenses are transfer-pad printed with the aqueous ink composition, the markings on the surfaces of the lenses formed when the ink composition dried. At room temperature, drying occurred within a few seconds or less when air is blown on the aqueous ink composition. The markings were easily removable with water.

While the invention has been described in terms of various preferred embodiments, the skilled artisan will appreciate the various modifications, substitutions, and changes which may be made without departing from the

spirit hereof. The descriptions of the subject matter in this disclosure are illustrative of the invention and are not intended to be construed as limitations upon the scope of the invention.

WHAT IS CLAIMED IS:

1. An aqueous coating composition suitable for use in transfer-pad printing comprises effective amounts of (a) a water soluble polymer; (b) an opacifier; and (c) a dispersant.

2. The composition of claim 1 wherein the water soluble polymer is selected from the group consisting of urethanes, acrylates, epoxies, cellulose derivatives, vinyl polymers and mixtures thereof.

3. The composition of any of claims 1-2 wherein the opacifier is selected from the group consisting of titanium dioxide, aluminum oxides, aluminum silicates, silica, and mixtures thereof.

4. The composition of any of claims 1-3 wherein the dispersant is selected from the group consisting of water-reducible alkyds, acrylics, polyesters, epoxies, and mixtures thereof.

5. The composition of any of claims 1-4 wherein the water soluble polymer comprises about 10% to about 30% of the composition.

6. The composition of any of claims 1-5 wherein the opacifier comprises about 5% to about 45% of the composition.

7. The composition of any of claims 1-6 wherein the dispersant comprises about 0.5% to about 5.5% of the composition.

8. The composition of any of claims 1-7 further comprising a colorant.

9. The composition of any of claims 1-8 further comprising a release agent.

10. The composition of any of claims 1-9 wherein the composition contains essentially no organic solvents.

11. A process of transfer-pad printing a pattern of a liquid coating from a cliché ink source onto a surface of an article wherein the liquid coating comprises an aqueous coating composition that comprises effective amounts of (a) a water soluble polymer; (b) an opacifier; and (c) a dispersant.

12. The process of claim 11 wherein the water soluble polymer is selected from the group consisting of urethanes, acrylates, epoxies, cellulose derivatives, vinyl polymers and mixtures thereof.

13. The process of any of claims 11-12 wherein the opacifier is selected from the group consisting of titanium dioxide, aluminum oxides, aluminum silicates, silica, and mixtures thereof.

14. The process of any of claims 11-13 wherein the dispersant is selected from the group consisting of water-reducible alkyds, acrylics, polyesters, epoxies, and mixtures thereof.

15. The process of any of claims 11-14 wherein the water soluble polymer comprises about 10% to about 30% of the composition.

16. The process of any of claims 11-15 wherein the opacifier comprises about 5% to about 45% of the composition.

17. The process of any of claims 11-16 wherein the dispersant comprises about 0.5% to about 5.5% of the composition.

18. The process of any of claims 11-17 wherein the composition further comprises a colorant.

19. The process of any of claims 11-18 which employs a silicone transfer pad and wherein the composition further comprises a release agent.

20. The process of any of claims 11-19 wherein the composition contains essentially no organic solvents.

21. An article of manufacture containing a transfer-pad printed design thereon, wherein the design is made by the process of any of claims 11-20.

22. The article of claim 21 wherein the water soluble polymer is selected from the group consisting of urethanes, acrylates, epoxies, cellulose derivatives, vinyl polymers and mixtures thereof.

23. The article of any of claims 21-22 wherein the opacifier is selected from the group consisting of titanium dioxide, aluminum oxides, aluminum silicates, silica, and mixtures thereof.

24. The article of any of claims 21-23 wherein the dispersant is selected from the group consisting of water-reducible alkyds, acrylics, polyesters, epoxies, and mixtures thereof.

25. The article of any of claims 21-24 wherein the water soluble polymer comprises about 10% to about 30% of the composition.

26. The article of any of claims 21-25 wherein the opacifier comprises about 5% to about 45% of the composition.

27. The article of any of claims 21-26 wherein the dispersant comprises about 0.5% to about 5.5% of the composition.

28. The article of any of claims 21-27 wherein the composition further comprises a colorant.

29. The article of any of claims 21-28 wherein said process employs a silicone transfer pad and wherein the composition further comprises a release agent.

30. The article of any of claims 21-29 wherein the composition contains essentially no organic solvents.

31. The article of any of claims 21-30 wherein the article is an ophthalmic lens made from glass.

32. The article of claim 31 wherein the ophthalmic lens includes (i) an abrasion resistance coating, (ii) an anti-reflection coating, or (iii) both an abrasion resistant coating and an anti-reflection coating.

33. The article of any of claims 21-30 wherein the ophthalmic lens comprises two lens wafers laminated together.

34. The article of claim 33 wherein the ophthalmic lens includes (i) an abrasion resistance coating, (ii) an anti-reflection coating, or (iii) both an abrasion resistant coating and an anti-reflection coating.

35. The article of claim 21 wherein the article is an ophthalmic lens made of plastic that is selected from the group consisting of poly(allyl diglycol carbonate), diacrylate, dimethylacrylate, and polycarbonate.

36. The article of claim 35 wherein the ophthalmic lens includes (i) an abrasion resistance coating, (ii) an anti-reflection coating, or (iii) both an abrasion resistant coating and an anti-reflection coating.

37. The article of any of claims 35-36 wherein the ophthalmic lens comprises two lens wafers laminated together.

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C09D 11/00; G02B 3/00, 1/06; C03C 17/00
US CL :106/31.6, 31.69, 31.27, 31.37; 359/642, 665; 523/160
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 106/31.6, 31.69, 31.27, 31.37; 359/642, 665; 523/160

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, search terms: polymers, resins, thermoplastic, opacifier, titanium dioxide, dispersant, dispersing agent, opthalmic lenses, glass, printing ink

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	US 5,523,335 A [WHYZMUZIS et al] 04 June 1996, col 2, lines 21-47, column 3, lines 3-4, column 5, lines 10-11, column 6, lines 53-54, and column 10, lines 1-10.	1-37

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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